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METHOD 506

I. SCOPE AND APPLICATION:

This method describes a procedure for the determination of certain phthalate and adipate esters in drinking water by either liquid/liquid or liquid/solid extraction. The following compounds can be determined using this method.

Analyte	Chemical Abstract Services Registry Numbers (CASRN)
Bis (2-ethylhexyl) phthalate	117-81-7
Butylbenzyl phthalate	85-68-7
Di-n-butyl phthalate	84-74-2
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
Bis (2-ethylhexyl) adipate	103-23-1
Di-n-octyl phthalate	117-81-7

II. REAGENTS:

- Sodium Thiosulfate ($Na_2S_2O_3$) solution

III. MATERIALS:

- 1-liter amber borosilicate sample bottle fitted with screw caps lined with TFE fluorocarbon.
- Pool and Spa 3-Way Test Strips (Chem Lab Products, Inc.)
- Latex gloves
- Paper towels
- Plastic container for disposal of used pipette tips
- Disposable glass pipette and rubber bulb.
- Kim wipes
- Pliers
- Protective Eyewear

IV. PROCEDURE:

1. Remove any attachments such as hoses, screens or aeration devices on the faucet. Inspect the faucet for anything that may fall into the sample container.

2. Open the tap and allow the system to flush for about 10 minutes. This should be sufficiently long enough to allow the water temperature to stabilize and get a representative sample.

3. Adjust the water flow to about 1000 ml/minute or slow enough that no air bubbles purge the sample when collecting from the flowing stream.

4. Remove the cap from the 1-liter container. Do not rinse the container as it has already been acid rinsed and may already contain sodium thiosulfate as a preservative.

5. To fill, tip the bottle to about a 45° angle into the stream of water. Ensure the stream is sufficiently slow so as to be able to anticipate when the bottle is nearly full and thus avoid over flowing. Fill the bottle to within approximately ½ inch of the mouth.

6. Remove the bottle from the flow and recap. Invert the sample bottle five times.

7. Place a chlorine detector strip on a dry opened paper towel. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Moisten the chlorine detector strip with using the aliquot and immediately flick the chlorine detector strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference chlorine range. A determination must be made within 30 seconds.

IV. PROCEDURE (continued):

8. If no chlorine is detected, recap the bottle firmly, dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Record the results in the field notebook and place the sample bottle in the ice chest to cool to 4°C.

9. If chlorine is present, add 5 drops of sodium thiosulfate solution, recap the bottle firmly and invert 5 times. Place a chlorine detector strip on a dry opened paper towel. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Thoroughly moisten the chlorine detector strip with the aliquot from the glass pipette and immediately flick the chlorine detector strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference chlorine range. A determination must be made within 30 seconds.

10. If no chlorine is detected, recap the bottle firmly, dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Record the results in the field notebook and place the sample bottle in the ice chest to cool to 4°C.

11. Continue the process of adding sodium thiosulfate to the sample, recapping, mixing, and testing until no chlorine is detected. Remember to note the number of drops of sodium thiosulfate added to the water sample in the field notebook.

V. SAMPLE TRANSPORT:

After obtaining the water samples, attach the completed chain of custody seal around the plastic cap of each 1-liter bottle. The 1-liter bottle must be amber colored to reflect sunlight since some of the pesticides analyzed for in this method are light sensitive and degrade when exposed to ultraviolet radiation. Place the sample bottle into the ice chest for transport. The samples must be chilled and preserved at a temperature of 4°C and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the semi-volatile samples for transportation. Never use “blue ice” as the samples may not chill adequately. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C upon arrival at the laboratory.

VI. SAMPLE PRESERVATION:

The samples must be iced or refrigerated at 4°C and protected from light from the time of collection until extraction. Limited holding studies have indicated that the analytes thus stored are stable for up to 14 days or even longer if preserved properly.

VII. DEFINITIONS:

A. *Sodium Thiosulfate ($Na_2S_2O_3$):* A preservative use to dechlorinate water samples. Reduces free chlorine into acid.

B. *Eluant:* The solvent that contains the analytes after extraction or desorption.

C. *LSE Cartridge:*Cartridges are inert nonleaching plastic and must not contain plasticizers such as phthalates and adipates. The cartridges are packed with about 1 gram of silica (or Teflon) whose surface is impregnated with chemically bonded octadecyl (C_{18} carbon groups).

VIII. SAFETY:

The use of protective eyewear and laboratory quality latex gloves is highly recommended when collecting and preserving samples.

IX. SUMMARY OF METHOD:

METHOD 506: liquid/liquid extraction--The sample volume is measured and spiked with a surrogate (and any target compounds for quality control purposes) then transferred into a 2-liter separatory funnel containing 50g of NaCl. The extraction process begins by adding 60 ml of methylene chloride to the sample bottle that is then capped and mixed to rinse the inner walls of the bottle and then transferred to a separatory funnel. The sample is extracted by shaking the separatory funnel for two minutes with periodic venting to release excess pressure. The organic layer is allowed to to separate from the water sample. The organic layer is removed and placed in an erlenmeyer flask. The process of salting, adding methylene chloride to the water sample, extraction, and separation of the organic layer is performed two more times. After each extraction, the methylene chloride extract is combined is combined in the erlenmeyer flask. The sample is then extracted a fourth time using just 40ml of hexane (no salt) and added to the erlenmeyer flask.

The entire contents of the erlenmeyer flask is is concentrated to approximately 10-20 ml using a Kuderna-Danish (K-D) concentrator (this is an evaporative process) and passed through a drying tube containing about 10 cm of pre-rinsed anhydrous sodium sulfate to remove water and collected in and evaporative flask. The drying column is rinsed with 20-30 ml of methylene chloride to remove any target compounds adhering to the drying tube and collected in the evaporative flask containing the “dried” extract which is then concentrated (evaporated) to a volume of 0.5 to 1.0 ml.

IX. SUMMARY OF METHOD (continued):

METHOD 506: liquid/solid extraction--The sample volume is measured and then transferred into a 2-liter separatory funnel with a solvent reservoir connected beneath it. The solvent resevoir has the liquid/solid extraction (LSE) cartridge attached below it and the LSE cartridge leads into a vacuum flask. As the sample passes from the separatory funnel through the LSE cartridge, the LSE cartridge extracts the target compounds from the water. The target compounds are then desorbed from the LSE cartridge first using acetonitrile and followed by methylene chloride and passed through an anhydrous sodium sulfate drying column. The "dried" eluant is then concentrated (evaporated) to a volume of 0.5 to 1.0 ml.

Once the extraction is complete, 2 µl of the extract is injected into the gas chromatograph and the analytes in the extract are separated in the column of a GC using a temperature programming The phthalate and adipate esters are then identified and quantitated using a photoionization detector (PID).